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ZEOLITE PREFILTER TO REDUCE PLUGGAGE IN ZEOLITE CESIUM REMOVAL COLUMN

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ABSTRACT

Pluggage has frequently necessitated premature replacement of zeolite used to remove ^{137}Cs from Savannah River Plant waste. This pluggage is likely caused by suspended solids in the column feed or by a precipitate formed by reaction of the waste and zeolite. Laboratory tests show that a 6-inch granular, backwashable prefilter made of zeolite reduces pluggage of the zeolite cesium removal column.

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INTRODUCTION

The Savannah River Plant uses "Linde"* AW-500 molecular sieve zeolite in cesium removal columns at waste storage facilities associated with fuel reprocessing plants. These columns remove ^{137}Cs from the overheads of evaporators used to concentrate aged radioactive waste. Also, waste solution from the regeneration of ion exchange resin is processed in the cesium removal column in one facility. Effluent from the column is released to seepage basins, and the spent zeolite is put in waste tanks.

Pluggage has necessitated premature replacement of the zeolite. Pluggage occurs most frequently in the facility processing waste solutions from the regeneration of ion exchange resins. This waste contains considerably more dissolved material than the evaporator overheads.

The following study was made to determine the cause of pluggage and to develop a means of preventing it.

SUMMARY

Evidence supports several possible causes of zeolite pluggage. The two most likely causes are suspended solids in column feed and a precipitate formed by reaction of the zeolite with the waste. Studies made with a laboratory zeolite column equipped with manometers show that nearly all pluggage occurs in the top 6 inches of the column. This suggested the use of a 6-inch column of zeolite as a granular, backwashable prefilter for the cesium removal columns. Laboratory tests show that this prefilter reduces pluggage of the cesium removal columns.

* Trademark of Union Carbide Corporation.

DESCRIPTION OF CRC SYSTEMS

The cesium removal column (CRC) systems (Figure 1) contain approximately 300 pounds of "Linde" AW-500 molecular sieve, a synthetic zeolite with high affinity for cesium.[2,3] The cylindrical column is 22 inches in diameter and 42 inches long. Its bottom is a cone of heavy gauge stainless steel perforated with 100-mesh-size holes. Flow through the column is downward at a rate of 5 to 10 bed volumes per hour. The effluent is monitored in a hold tank before release to seepage basins. The concentration of ^{137}Cs in CRC effluent is normally less than 1% of that in CRC feed.

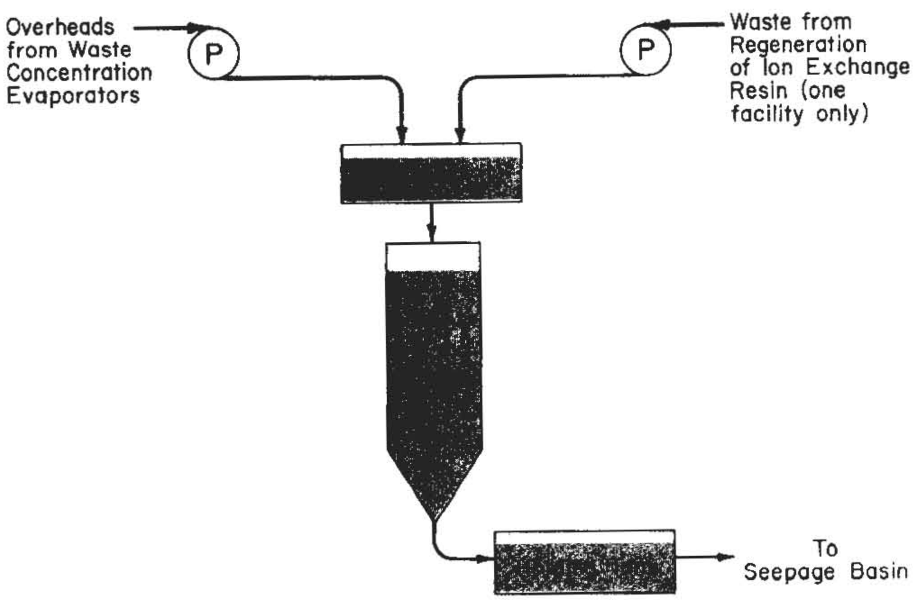

FIG. 1 SCHEMATIC OF THE CRC SYSTEMS

EXPERIMENTS

To study the pluggage problem, a laboratory model CRC system was assembled. The laboratory column was made of 1-inch-inside-diameter "Plexiglas"* tubing to hold a 42-inch-long bed of zeolite - the same length as the CRC in the processing facilities. The bottom screen was made of the same perforated stainless steel plate as used in the CRC. The column was filled with 20-50 mesh "Linde" AW-500 zeolite. Column feed was waste from regeneration of ion exchange resin, which has produced serious pluggage. A flow rate of 10 bed volumes per hour through the column was maintained until a feed pressure of 7.5 psi was required to obtain this flow. Then as pluggage increased the flow was allowed to decrease.

Location of Pluggage

To determine whether pluggage occurred throughout the column or was limited to a specific zone, manometers were installed at 6-inch intervals in the column. Pressure drops across each 6-inch interval were measured on six different columns receiving waste from regeneration of ion exchange resin, all of which became plugged before breakthrough of ^{137}Cs. The results shown in Figure 2 represent a typical column operated at constant feed pressure of 7.5 psi. Pressure drop changes in the top 6 inches of the column greatly exceeded changes in the remainder of the column. In the top 6 inches, the pressure drop increased from an initial value of 8 inches of water to 64 inches of water after 40 bed volumes. The column flow was then stopped overnight. The next morning the pressure drop was only 10 inches of water but rapidly increased to 380 inches of water by 80 bed volumes total flow. In comparison, after 80 bed volumes, the pressure drop across the second 6-inch section (6 to 12 inches) had increased to only 48 inches of water, and across the remaining 30 inches (12 to 42 inches) the pressure drop was only 27 inches of water. The perforated plate was in the 36- to 42-inch section of the column and showed no evidence of pluggage. These data show that pluggage is largely confined to the top 6 inches of the column.

* Trademark of Rohm and Haas Company

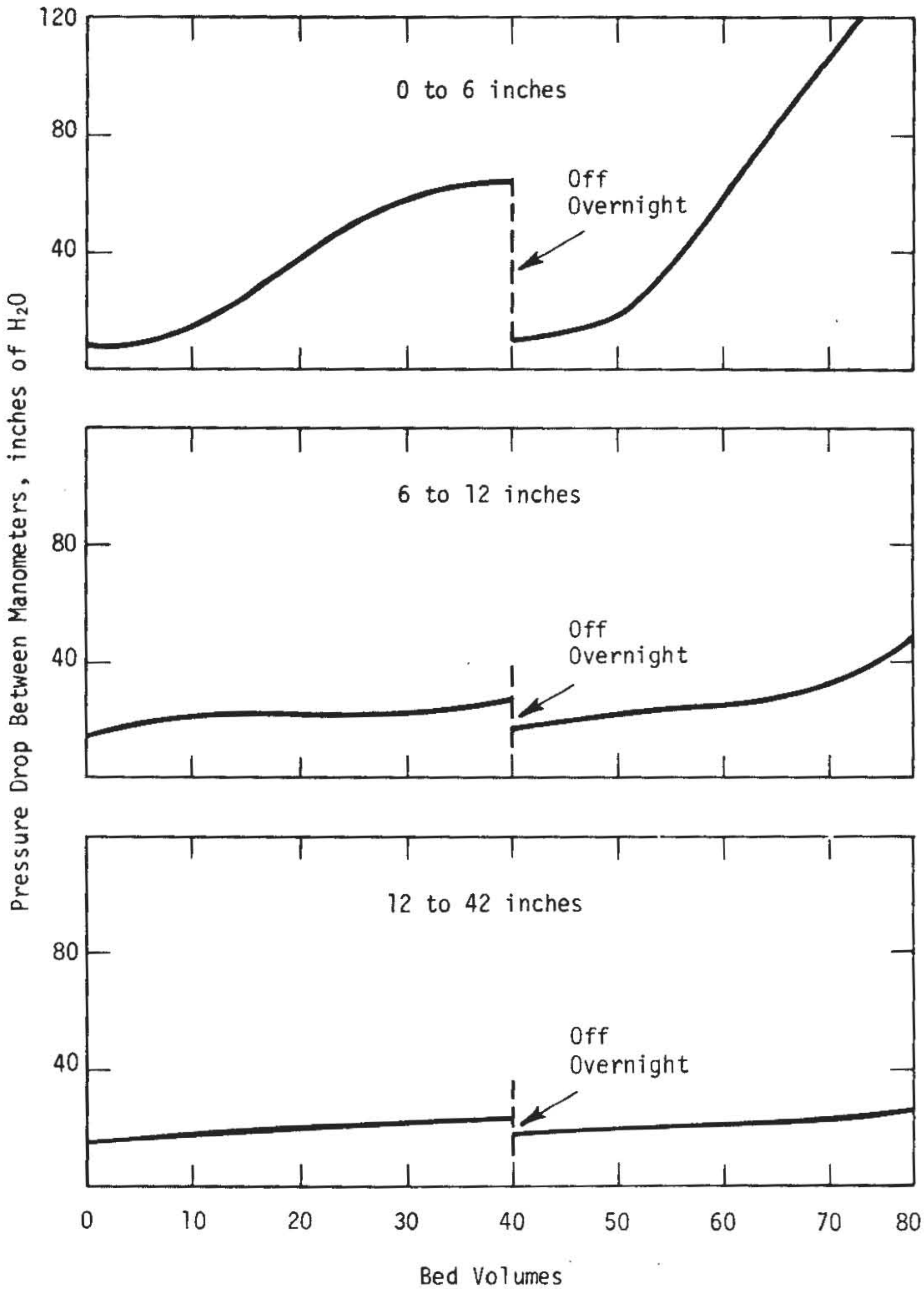

FIG. 2 PRESSURE DROP CHANGES IN ZEOLITE COLUMN

Causes of Pluggage

Evidence supports several factors as possible causes of column pluggage. In one laboratory zeolite column, a filamentous mass was observed in the top one inch of a plugged column. The mass was identified as Aspergillus Glaucus, a fungus that can survive severely unfavorable conditions and grow rapidly when conditions become favorable. The cause of pluggage in this one column was clearly the fungus growth. However, it has not occurred in other laboratory columns, and fungus is now considered an improbable cause of CRC pluggage in the plant columns.

In 1968, the perforated plate in the bottom of the column in the area processing both overheads and regeneration waste solutions was removed because of suspected damage. A coating of white salt was found attached firmly to the lower third of the conical plate. Although the perforations were not fully closed by the deposit, flow was restricted. The salt was identified as Na_2CO_3, but its presence on the perforated plate could not be explained. No deposits have been found on the perforated plates in numerous laboratory columns. Hence salt deposits on the perforated plate are considered an improbable cause of CRC pluggage.

Fines from the degradation of "Linde" AW-500 zeolite have been suggested as a cause of pluggage. It has been observed that some fines are usually present and can be removed from a column by upflow operation or backwashing. The source of fines is physical disintegration of the zeolite particles, which have relatively little wet strength. The filtering action of a column could accumulate fines sufficient to cause pluggage. However, since the fines would originate throughout the length of the column, pluggage due to fines should occur in the middle or lower part of the column during downflow operation. Pluggage was observed only in the top 6 inches of laboratory columns during downflow operation, and hence could not result from zeolite fines released by the column.

Two remaining possible sources of pluggage are suspended solids in the feed liquid, and a fine, white precipitate frequently present on the top surface of columns after operation. One or both of these probably account for most CRC pluggage.

To determine whether solids were present in CRC feed, 31 column feed samples were collected from two facilities during a two-week period. Each sample was filtered through a preweighed 0.45-μ pore-size "Millipore"* filter. Results were as follows:

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* Trademark of the Millipore Corporation, Bedford, Mass.

14 Samples (Overheads only)	3 - No solids 9 - Trace 2 - 25 mg/l avg
17 Samples (Overheads plus regeneration waste)	0 - No solids 12 - Trace 5 - 32 mg/l avg

Since it had been previously observed that column effluent samples contained no filterable solids, these data indicate column feed sometimes carries suspended solids which remain in the column causing pluggage.

A fine, white precipitate has been observed frequently on the upper zeolite surface of a used column, but has not been observed at depth in the column. A similar precipitate can be formed by mixing zeolite with the waste from regeneration of ion exchange resin; the amount of precipitate appears to depend on the amount of zeolite present. Initially the precipitate is light and flocculent, resembling $Al(OH)_3$, but in time it becomes compacted. Some batches of the waste solutions produce little or no precipitate.

Samples of the precipitate were collected from used columns, and the dried samples were analyzed by emission spectroscopy, spark source mass spectroscopy, and X-ray diffraction to determine their composition. Results showed the samples were high in sodium, calcium, oxygen, phosphorus, and silicon, suggesting sodium and calcium phosphates and silicates. No specific compound was indicated, however, even by X-ray diffraction.

Because the precipitate was formed when zeolite and waste solution were brought together, its composition must be derived from one or both of these materials. "Linde" AW-500 zeolite is a hydrated aluminum silicate containing some sodium and calcium. A typical composition of waste solution from regeneration of ion exchange resin is:

pH	- 11 to 12
Na^+	- 3600 ppm (0.15N)
NO_3^-	- 2000 ppm (0.03N)
Cr (as CrO_4^{-2})	- 46 ppm
P (as PO_4^{-3})	- 20 ppm
K^+	- 14 ppm
Cs^+	- 0.4 ppb
^{137}Cs	- 9×10^4 dis/(min)(ml)

Thus, the elements found in the precipitate are present in AW-500 zeolite and waste from regeneration of ion exchange resin.

Removal of Materials that Cause Pluggage

Several types of filters were tested to remove suspended solids carried by waste from regeneration of ion exchange resins. Sand filters appeared to have ample capacity but failed to provide adequate filtration since fine solids were present in the sand filter effluent. Three relatively high performance filters did produce solids-free effluent: "Millipore" 0.45-μ pore size disks, Whatman* number 5 paper disks, and Pall** 1-μ pore size corrugated cartridge filters. However, rapid pluggage of these filters necessitated too frequent replacement for practical operation. Moreover, filtration would not prevent pluggage from the precipitation reaction unless the precipitation occurred ahead of the filter.

The studies that showed that pluggage occurs in the top 6 inches of the zeolite column suggested prefiltration using a prefilter of zeolite. Such a prefilter should not only remove suspended solids from feed but should also provide a site for the precipitation reaction to occur ahead of the column. Laboratory tests showed that a prefilter of 20-50 mesh AW-500 zeolite 6 inches long effectively removed suspended solids from the waste from regeneration of ion exchange resins. Tests also showed that the white precipitate formed and was held in the zeolite prefilter with only traces occurring in the 42-inch cesium removal column. It was further observed that when the prefilter became plugged, backwashing by reverse flow with waste readily restored the effectiveness of the prefilter.

In the CRC system, a prefilter between the pump and the 42-inch column consists of a "Plexiglas" column 1 inch in inside diameter and 6 inches long, filled with 20-50 mesh "Linde" AW-500 zeolite. The column was operated at 10 bed volumes per hour with resin regeneration waste fed to it at a maximum pressure of 7.5 psi. The pressure drop was measured across the 6-inch prefilter and also across the 42-inch laboratory CRC during 2000 bed volumes throughput. These results are shown in Figure 3.

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* W. and R. Balston, Ltd., Maidstone, England.
** The Pall Trinity Micro Corporation, Glen Cove, L.I., N. Y.

The pressure drop across the prefilter increased and was relieved through 6 cycles of operation and backwash. Backwashing was by reverse flow of water through only the prefilter at 14 bed volumes per hour for one minute. This fluidized the zeolite bed and removed the fine particulate material and white precipitate present in the upper part of the prefilter bed.

In previous tests, 42-inch columns receiving unfiltered feed developed pressure drops of more than 6.8 psi before 500 bed volumes throughput. As shown in Figure 3, the pressure drop across the 42-inch column receiving filtered feed increased slowly from 3.5 psi initially to 6.8 psi at 2000 bed volumes throughput. The flow rate did not fall below the intended 10 bed volumes per hour before 1500 bed volumes throughput, and was 6 bed volumes per hour at 2000 bed volumes.

To more clearly determine the effectiveness of zeolite prefiltration, two laboratory CRC systems were operated simultaneously from one feed supply. One CRC system consisted of only a zeolite column 1 inch in diameter and 42 inches long. The other CRC system was like the first but included a zeolite prefilter 1 inch in diameter and 6 inches long. Results are shown in Figure 4.

The feed pressure of 7.5 psi was more than adequate to maintain flow of 10 bed volumes per hour through both columns initially. Although the column receiving unfiltered feed plugged rapidly and its flow rate was near zero at 390 bed volumes, flow through the column receiving filtered feed was still at 6 bed volumes per hour at 1230 bed volumes. The prefilter was backwashed five times during the 1230 bed volumes. This comparative test demonstrated that the prefilter effectively reduced pluggage and greatly lengthened the useful life of a CRC.

Comparison of the data in Figures 3 and 4 also illustrates the variability of resin regeneration waste solutions in producing column pluggage. One column receiving filtered feed maintained 10 bed volumes per hour through 1500 bed volumes, and the prefilter required only six backwashes through 2000 bed volumes (Figure 3). Another column also received filtered feed and was similar to the previous column in every way, yet it maintained 10 bed volumes per hour through only 410 bed volumes throughput and its prefilter required three backwashes during the first 440 bed volumes and none during the last 960 bed volumes (Figure 4). Because the feed for these columns was obtained from different batches of resin regeneration waste, the difference in column performance is attributed to variability in the feed composition.

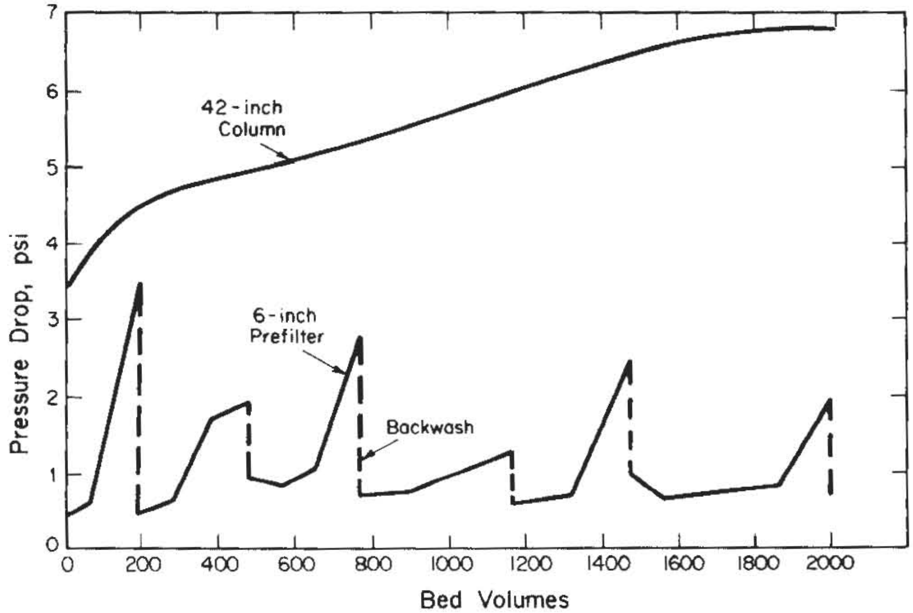

FIG. 3 PRESSURE DROP ACROSS ZEOLITE PREFILTER AND COLUMN

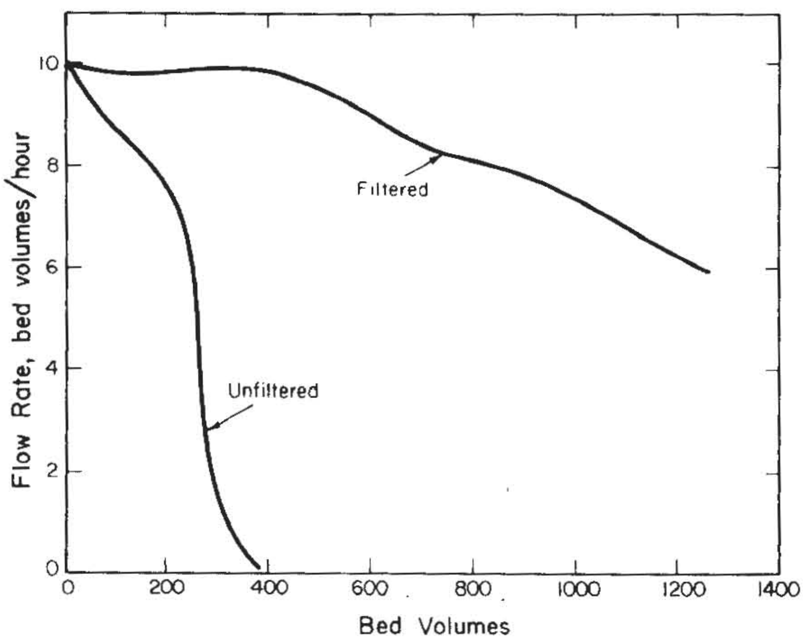

FIG. 4 FLOW RATES THROUGH ZEOLITE COLUMNS WITH AND WITHOUT A ZEOLITE PREFILTER

To observe any loss of efficiency after prolonged use of a zeolite prefilter, a new zeolite prefilter was compared with an old one in a test. Two 42-inch zeolite columns were operated simultaneously from the same liquid feed system. One column was served by a new prefilter containing a 6-inch depth of unused 20-50 mesh AW-500 zeolite. The other column was served by an old prefilter containing a 6-inch depth of 20-50 mesh AW-500 zeolite that had previously received 6500 bed volumes and 29 backwashes. Results are shown in Figure 5.

The data show similar flow rates through the two columns. Both prefilters were backwashed as needed, this being four times each. Both columns showed some gradual reduction in flow rate from 10 initially to 6 bed volumes per hour after 2000 bed volumes throughput. The small difference in flow rate between the two columns at any time probably reflects unavoidable, but slight, differences in zeolite bed packing in the columns. There appeared to be no effect due to differences between the old and new zeolite prefilters.

Based on the results and experience of this study, a 6-inch-long AW-500 zeolite prefilter would significantly improve CRC operation. Radiation shielding should be provided wherever personnel work near the prefilter, because the zeolite charge will sorb considerable ^{137}Cs during extended use and should last indefinitely unless lost through improper operation.

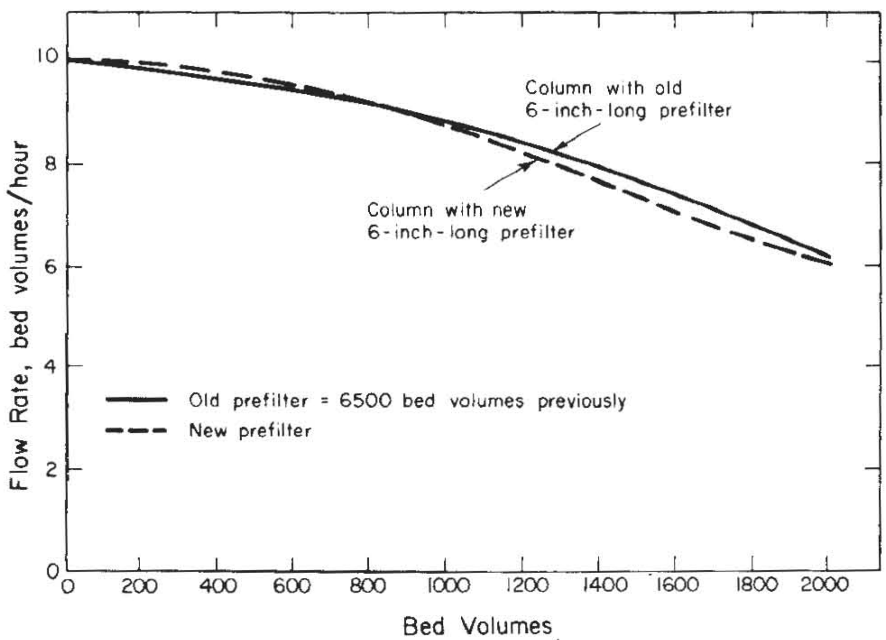

FIG. 5 FLOW RATES THROUGH TWO 42-INCH-LONG ZEOLITE COLUMNS TO COMPARE OLD AND NEW ZEOLITE PREFILTERS

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